

## Effects of Silica on the Formation of Epoxidised Natural Rubber/Polyvinyl Chloride Membrane

(Kesan Pengisi Silika ke Atas Pembentukan Membran Getah Asli Terepoksida/Polivinil klorida)

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### ABSTRACT

*The presence of pores plays an important role for many membrane processes especially in ultrafiltration and microfiltration. Epoxidised natural rubber (ENR)/polyvinyl chloride (PVC) membranes filled with two types of silica fillers were prepared via simultaneous solvent exchange and evaporation of solvent technique. Two types of silica, i.e. microsilica (microcrystalline silica powder) and nanosilica (generated from tetraethoxysilane (TEOS)) were used. The chemical composition, morphology and mechanical stability of the membranes were studied. Both types of silica showed good interaction with the membrane matrix. The formation of pores depended on the size of silica particles added. Microsilica produced large pores while in-situ generated nanosilica produced nanosized pores. The mechanical properties of membrane improved with the addition of silica. The tensile strength increased from 10.6 MPa to 17.8 MPa and 14.5 MPa for nanosilica and microsilica filled membrane while the tensile modulus increased from 1.6 MPa to 3.8 MPa and 3.4 MPa, respectively. Thus, both types of silica acted as a filler as well as pore forming agent for the ENR/PVC membrane.*

**Keywords:** Epoxidised natural rubber; polyvinyl chloride; pore forming agent; silica; tetraethoxysilane

### ABSTRAK

*Kehadiran liang memainkan peranan penting dalam kebanyakan proses bermembran terutamanya dalam aplikasi penurasan ultra dan penurasan mikro. Membran getah asli terepoksida (ENR)/polivinil klorida (PVC) terisi dua jenis pengisi silika yang dihasilkan melalui penukaran pelarut dan penyejatan secara spontan. Dua jenis silika digunakan iaitu mikrosilika (serbuk kristal mikrosilika) dan nanosilika (dihasilkan daripada Tetraetoksilana (TEOS)). Komposisi kimia, morfologi dan kestabilan mekanik membran telah dikaji. Kedua-dua jenis silika menunjukkan interaksi yang baik dengan matriks membran. Pembentukan liang bergantung kepada saiz silika yang digunakan. Mikrosilika menghasilkan liang yang besar manakala nanosilika yang terjana secara in-situ menghasilkan liang nano. Sifat mekanik membran menunjukkan peningkatan dengan penambahan silika. Kekuatan tensil bertambah daripada 10.6 MPa kepada 17.8 MPa dan 14.5 MPa untuk membran berpengisi nanosilika dan mikrosilika, manakala tensil modulus bertambah daripada 1.6 MPa kepada 3.8 MPa dan 3.4 MPa untuk setiapnya. Oleh itu, kedua-dua jenis silika bertindak sebagai penguat dan juga agen penjana liang untuk membran ENR/PVC.*

**Kata kunci:** Agen penjana liang; getah asli terepoksida; polivinil klorida; silika; tetraetoksilana

### INTRODUCTION

In filtration technology, membrane is a layer of material that serves as a selective barrier between two phases (Mulder 2000). The utilization of membrane as separation agent is more efficient as compared with conventional separation process (Abdul Wahab 2010). Membrane process has extensively been applied in many applications such as microfiltration, reverse osmosis, hemodialysis, ultrafiltration, electrodialysis and gas separation (Mohd Salleh 1990; Mulder 2000). Membranes can be made from organic (polymer) and inorganic (ceramic) materials (Mulder 2000). The development of new membrane materials will be determined by the specific properties of the membrane to be compatible for applications.

Porosity is an important feature of membranes (Van de Witte et al. 1996) especially for wastewater treatment. An ideal membrane for separation process must be porous and mechanically stable to maintain the life of the membrane as well as enhancing membrane selectivity and flux. Many researchers have studied the effect of addition of inorganic particles like silica, titania and zirconia in membrane fabrication process (Arthanareeswaran et al. 2009; Arthanareeswaran & Thanikaivelan 2010; Chen et al. 2010; Hu et al. 1997; Yu et al. 2009). An addition of additives or inorganic particles into casting solution during membrane making process will help to create or enhance the pores (Arthanareeswaran et al. 2009) and increase the mechanical properties of the membrane.

Arthanareeswaran et al. (2009) studied the effect of addition of silica ( $\text{SiO}_2$ ) in cellulose acetate (CA) membrane and found that porosity and mechanical stability of CA/ $\text{SiO}_2$  membrane had increased. Silica may exist in many forms and sizes. Nanosilica can be generated through sol-gel process. The process involves repeated hydrolysis and condensation steps of silica precursor (tetraethoxysilane (TEOS)) under appropriate chemical condition (Brinker & Scherer 1990).

Mechanical stability is very important especially for non-support membranes and for applications involving high pressures (Mulder 2000). The structure of a membrane filtration system consists of two layers; selective layer and support layer. The upper selective layer is thin and usually brittle which requires a porous support layer. This will increase the cost of membrane fabrication process.

It is important to prepare a porous membrane that is self-supported in order to minimize the preparation cost. In this study, we attempted to prepare a self-supported porous membrane made from a blend of epoxidised natural rubber (ENR) and polyvinyl chloride (PVC). ENR is a hydrophilic elastomer with high shearing and flexibility (Ibrahim 2000; Ibrahim & Dahlan 1998). PVC was chosen since it is a thermoplastic with solvent resistance and good mechanical properties. ENR and PVC can form a miscible blend (Ibrahim 2000). Normally, membrane made from rubbery materials such as natural rubber is non-porous. Hence, by adding the inorganic filler to the ENR and PVC blend, a porous and flexible membrane can be developed.

Various techniques can be used to prepare membranes. The common techniques are phase inversion (solvent exchange), evaporation of solvent (solution casting), track-etching, sol-gel process and vapor deposition (Beaker 2000; Liu et al. 2004). The ENR/PVC membrane was prepared by using simultaneous solvent exchange and evaporation technique. In this paper, the effects of two different types of silica, nanosilica and microsilica, on morphology and mechanical stability of the ENR/PVC membrane were studied. The roles of silica as filler and pore forming agent were discussed.

## MATERIALS AND METHODS

### MATERIALS

Epoxidised natural rubber (50% epoxidation) (ENR-50) and polyvinyl chloride (PVC) were supplied by Lembaga Getah Malaysia and Sigma Aldrich, respectively. Tetrahydrofuran (THF), toluene, tetraethoxyorthosilane (TEOS), hydrochloric acid (HCl) and microcrystalline silica powdered were purchased from System.

### PREPARATION METHODS

#### PREPARATION OF ENR/PVC MATRIX

A (60:40) ENR/PVC blends by weight percent was prepared using an internal mixer Brabender Plasticoder PL 2000.

The melt blending was carried out at  $160^\circ\text{C}$ . ENR-50 was charged into the mixing chamber at 10 rpm for 3 min for drying followed by addition of PVC for the next 10 min at 50 rpm.

### PREPARATION OF MEMBRANES

ENR/PVC matrix was dissolved in the mixture of THF and toluene in the proportion of 97.5:2.5 (% v/v) for 24 h at the matrix to solvent ratio 1:8 (w/v). The swelled ENR/PVC was then stirred for another 24 h using a magnetic stirrer. For the preparation of ENR/PVC/ $\text{SiO}_2$  membrane, 5% microcrystalline  $\text{SiO}_2$  powder (45  $\mu\text{m}$ ) was added into the ENR/PVC polymer solution and stirred for another 24 h for homogenization. The polymer solutions were left undisturbed for about 30 min to release the air bubbles. The solutions were spread on the surface of water by using a syringe. In the case of ENR/PVC/TEOS membrane, 25% of TEOS was added into the polymer solution. After 24 h of homogenization and 30 min of deaeration, the polymer solution was spread on the HCl acid/water (pH 1). Acidic medium was chosen to generate nanosilica from TEOS based on the work done by Bandyopadhyay et al. (2006). The membrane was then collected and washed with deionized water. All the membranes were dried at room temperature for 5 days prior to analysis.

## CHARACTERIZATION

### FTIR STUDY

The Fourier transform infrared spectroscopy (FTIR) spectra of the membranes were obtained using Perkin Elmer (GX FTIR System) in the wavenumber range of 400-4000  $\text{cm}^{-1}$ . The functional groups of the membranes were then deduced.

### MORPHOLOGICAL STUDIES

The top surface and cross section morphologies of membranes were observed by scanning electron microscope (SEM) (LEO 1450VP). The membranes were fractured in liquid nitrogen and sputter coated with gold to provide conductivity to the membranes.

### MECHANICAL STUDIES

The mechanical properties of the membranes were determined by using Universal Testing Machine (Instron 5566). The pulling rate of the sample was set at 50 mm/min. Four dumbbell shaped samples of 12 mm wide and 75 mm gauge length were cut out for each membrane.

## RESULTS AND DISCUSSION

### FTIR ANALYSIS

Figure 1 shows the FTIR spectra of ENR/PVC, ENR/PVC/ $\text{SiO}_2$  and ENR/PVC/TEOS membranes. All membranes show

similar absorptions in the range of  $3000\text{ cm}^{-1}$  to  $2800\text{ cm}^{-1}$  attributed to C-H stretching and  $1460\text{ cm}^{-1}$  to C-H bending (Bandyopadhyay et al. 2006). The characteristic bands for asymmetric vibrations of C-O-C (epoxy ring) occur at  $1254\text{ cm}^{-1}$  and  $874\text{ cm}^{-1}$  (Bandyopadhyay et al. 2006; Klinklai & Kunyawut 2009; Thongnuanchan et al. 2007). C-Cl absorption peak from PVC is also observed at  $699\text{ cm}^{-1}$ .

The presence of silica in both ENR/PVC/SiO<sub>2</sub> and ENR/PVC/TEOS membranes was confirmed with the existence of Si-O-Si asymmetric stretching at the absorption peaks of  $836\text{ cm}^{-1}$  and  $475\text{ cm}^{-1}$ , respectively (Muhammad Ali 2007). The presence of silanol (Si-OH) at  $966\text{ cm}^{-1}$  in both membranes was also detected. However, the presence of the Si-O-Si stretching vibration peak at  $1102\text{ cm}^{-1}$  in ENR/PVC/SiO<sub>2</sub> and  $1088\text{ cm}^{-1}$  in ENR/PVC/TEOS seemed to overlap with the wide vibration adsorption of C-O (epoxy group) symmetric stretching vibrations of ENR in the range of  $1110\text{--}1000\text{ cm}^{-1}$ . Peak at  $3466\text{ cm}^{-1}$  indicates the presence of OH peak. OH peak in both ENR/PVC/SiO<sub>2</sub> and ENR/PVC/TEOS membranes were less prominent as compared with ENR/PVC membrane because of the interaction with the silica added.

#### MORPHOLOGIES OF MEMBRANES

Figure 2 shows the SEM images of the surface and cross-section of each membrane. It was clearly seen that there were pores generated in ENR/PVC/SiO<sub>2</sub> and ENR/PVC/TEOS membrane in contrast to the control ENR/PVC membrane. Large pores generated in ENR/PVC/SiO<sub>2</sub> membrane as a result of the microsilica used. The pore size is smaller than the silica filler size due to shrinking on dislocation of the filler particle. On the other hand, small pores were

created in ENR/PVC/TEOS membrane due to the addition of nanosilica. During the membrane formation, some of the solvent (THF) evaporated from top surface of the membrane and the remaining solvent will diffuse into the water (Liu et al. 2004). The distribution of silica in the membranes (Figure 2(b) and 2(c)) appears to be relatively homogeneous and this showed that there is a strong silica and polymer interaction. The generation of pores may be due to high affinity of silica towards water (Wei et al. 2008). Some of the silica particles together with the solvent diffuse into water bath and create the pores. Inorganic fillers may function as a pore forming agent during simultaneous solvent exchange and evaporation processes (Chen et al. 2010). The thickness of the membrane formed was in the range of  $41\text{ }\mu\text{m}$  to  $64\text{ }\mu\text{m}$ . The membranes were relatively thin. However, a few layers of membrane can be laminated to be used under pressurized condition. Membrane of poly(ether block amide) (PEBA) of comparable thickness was also reported by Liu et al. (2004) using similar technique in the preparation of membranes.

#### MECHANICAL STUDY

The results of mechanical study of the membranes were listed in Table 1. It can be observed that the mechanical properties of the ENR/PVC membrane enhanced with the addition of silica. ENR/PVC/SiO<sub>2</sub> and ENR/PVC/TEOS membranes showed 37% and 68% increase in tensile stress and 108% and 131% in tensile modulus respectively, with respect to unfilled ENR/PVC membrane. The enhancement in mechanical properties was due to the good distribution of inorganic filler in the polymer

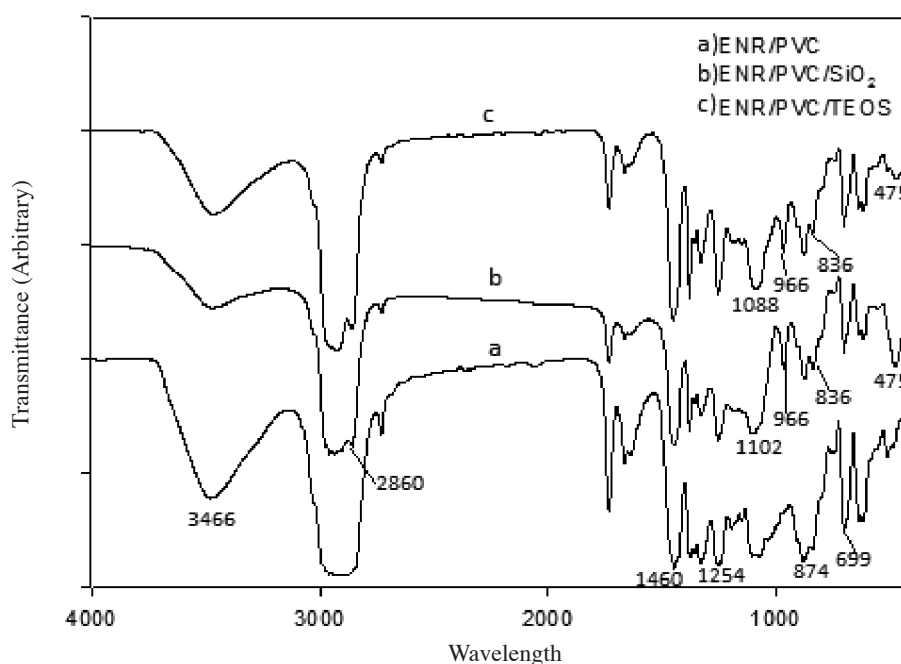


FIGURE 1. FTIR spectra for a) ENR/PVC, b) ENR/PVC/SiO<sub>2</sub> and c) ENR/PVC/TEOS

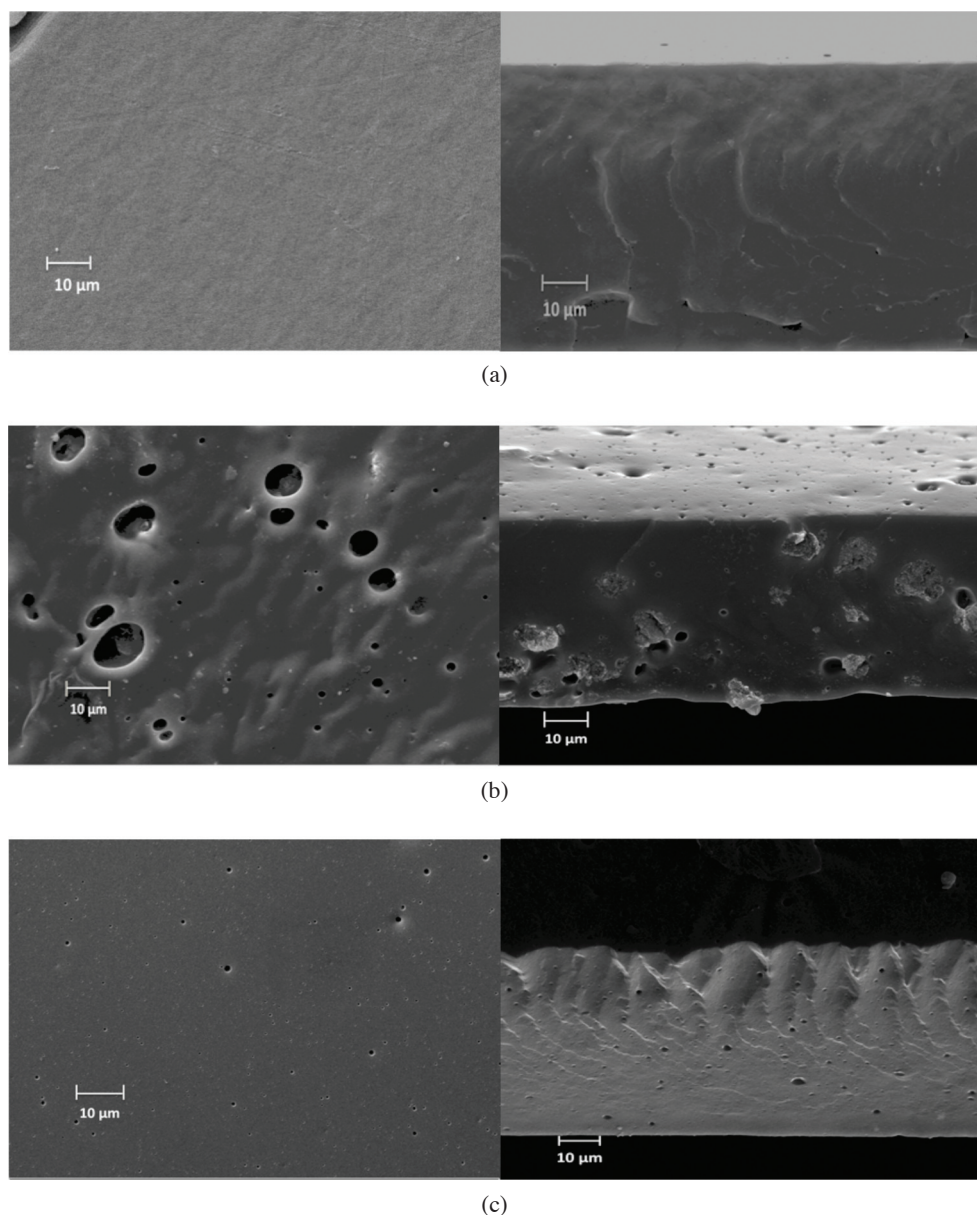


FIGURE 2. SEM images of surface and cross section of a) ENR/PVC; b) ENR/PVC/SiO<sub>2</sub> and c) ENR/PVC/TEOS

TABLE 1. Mechanical study of ENR/PVC membranes

Samples	Tensile Strength (MPa)	Tensile Modulus (MPa)
ENR/PVC	10.6	1.6
ENR/PVC/SiO <sub>2</sub>	14.5	3.4
ENR/PVC/TEOS	17.8	3.8

matrix as shown in Figure 2(b) and 2(c). ENR/PVC/SiO<sub>2</sub> membrane produced lower strength of both tensile stress and modulus as compared with ENR/PVC/TEOS membrane since the pores generated in the ENR/PVC/SiO<sub>2</sub> membrane were larger in size than the pores generated in the ENR/PVC/TEOS membranes. The increase of the free volume lowers the mechanical strength of the membrane.

#### CONCLUSION

Porous membrane made of ENR/PVC can be prepared using simultaneous solvent exchange and evaporation of solvent technique. Large pores can be obtained with the addition of microsilica (SiO<sub>2</sub> microcrystalline powder) whereas small pores with the *in-situ* generated nanosilica (TEOS). Mechanical and morphological studies of the membranes



showed that inorganic particles can function as filler as well as pore forming agent.

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